PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 43225-62465AWOP	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/US 03/10844	International filing date *(day/month/year)* 09.04.2003	Priority date *(day/month/year)* 12.04.2002
International Patent Classification (IPC) or both national classification and IPC C08F210/02		
Applicant DOW GLOBAL TECHNOLOGIES INC.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 4 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 5 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the opinion
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
11.11.2003	16.07.2004
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Simmerl, R Telephone No. +49 89 2399-8515

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US 03/10844

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

1-10, 12-23, 25-47, 49-64	as originally filed
11, 24, 48	filed with telefax on 11.06.2004

Claims, Numbers

1, 3-15	filed with telefax on 11.06.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).

   ☐ the language of publication of the international application (under Rule 48.3(b)).

   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority in written form.

   ☐ furnished subsequently to this Authority in computer readable form.

   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:

   ☐ the claims, Nos.:

   ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1,3-15
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1,3-15
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1,3-15
	No:	Claims	

2. Citations and explanations

see separate sheet

Ad section V.:

1. The present set of claims is novel over the prior art documents (Art. 33(2) PCT) cited in the search report. None of these documents mentions linear copolymers of ethylene and vinyl aromatic monomer as defined in claim 1 where said copolymers have a first terminal end group which is methyl and a second terminal end group which is a vinyl group.

2. The present set of claims is based on an inventive step (Art. 33(3) PCT).
The closest prior art document is (D1), EP-A-0 727 446 which describes branched copolymers. (D1) does not suggest the linear copolymers of present claim 1.

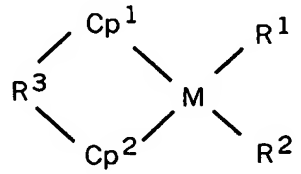
3. Industrial Applicability (Art. 33(4) PCT): o.k.

4. Additional remark:

   The description has not been adapted to the present set of claims. Claim 1 now claims linear copolymers with an ethylenically unsaturation at one terminal end but no longer only copolymers of ethylene and vinyl aromatic monomer having a molecular weight of less than 15 000 (Art. 6 PCT).

geometry catalysts in combination with various cocatalysts. Preferred operating conditions for such polymerization reactions are pressures from atmospheric up to 3000 atmospheres and temperatures from -30°C to 200°C. Polymerizations and unreacted monomer removal at temperatures above the autopolymerization temperature of the respective monomers may result in formation of some amounts of homopolymer polymerization products resulting from free radical polymerization. Additional methods are disclosed in U.S. Patent No. 6,344,515. Examples of suitable catalysts and methods for preparing the substantially random interpolymers are disclosed in U.S. Application Serial No. 702,475, filed May 20, 1991 (EP-A-514,828); as well as U.S. Patents: 5,055,438; 5,057,475; 5,096,867; 5,064,802; 5,132,380; 5,189,192; 5,321,106; 5,347,024; 5,350,723; 5,374,696; 5,399,635; 5,470,993; 5,703,187; and 5,721,185.

The substantially random α-olefin/vinyl aromatic interpolymers can also be prepared by the methods described in JP 07/278230 employing compounds shown by the general formula



where Cp^1 and Cp^2 are cyclopentadienyl groups, indenyl groups, fluorenyl groups, or substituents of these, independently of each other; R^1 and R^2 are hydrogen atoms, halogen atoms, hydrocarbon groups with carbon numbers of 1-12, alkoxyl groups, or aryloxyl groups, independently of each other; M is a group IV metal, preferably Zr or Hf, most preferably Zr; and R^3 is an alkylene group or silanediyl group used to cross-link Cp^1 and Cp^2).

The substantially random α-olefin/vinyl aromatic interpolymers can also be prepared by the methods described by John G. Bradfute et al. (W. R. Grace & Co.) in WO 95/32095; by R. B. Pannell (Exxon Chemical Patents, Inc.) in WO 94/00500; and in Plastics Technology, p. 25 (September 1992).

Also suitable are the substantially random interpolymers which comprise at least one α-olefin/vinyl aromatic/vinyl aromatic/α-olefin tetrad disclosed in U. S. Application No. 08/708,809 filed September 4, 1996 and WO 98/09999 both by Francis J. Timmers et al. These interpolymers contain additional signals in their carbon-13 NMR spectra with intensities greater than three times the peak to peak noise. These signals appear in the chemical shift range 43.70 - 44.25 ppm and 38.0 - 38.5 ppm. Specifically, major peaks are observed at 44.1, 43.9, and 38.2 ppm. A proton test NMR experiment indicates that the

Acrylic systems, while stable to oxygen and ultraviolet light, are inferior to diene-based elastomer systems in terms of the balance of tack, peel and creep resistance which is preferred for pressure sensitive adhesive applications. Further, such systems are typically available only in the solvent-based and water-borne systems, making them further disadvantageous for the reasons set forth above.

Hydrocarbon-based systems were developed at least in part to provide improved stability to oxygen and ultraviolet light, as compared to diene-based elastomer systems, as well as the ability to be utilized in hot melt adhesive systems. Hydrocarbon-based systems which comprise, atactic polypropylene, interpolymers of propylene with higher order alpha-olefins, or poly-alpha-olefins, exhibit a poor balance of properties. In particular, poly-1-butene has a tendency to slowly crystallize after application to the substrate, leading to a profound loss of tack. When oil is added to increase tack, the oil tends to migrate out of the adhesive into the backing layer or the substrate. Atactic polypropylene and poly-alpha-olefins suffer from low tensile strength, which leads to low cohesive strength on peel and to the leaving of a residue on the substrate surface after peeling. Hydrocarbon-based systems are typically not preferred due to the limited ability of low density polyethylene to accept the formulation ingredients required to produce a hot melt adhesive with suitable mechanical properties.

Ethylene vinyl acetate based systems are limited in that as higher vinyl acetate levels are selected, elastic performance increases, but compatibility with formulation ingredients decreases.

Hot melt adhesives based on homogeneous linear ethylene/alpha-olefin copolymers are disclosed in U.S. Pat. No. 5,530,054. Preferred hot melt adhesives based on homogeneous linear and substantially linear ethylene/alpha-olefin interpolymers are disclosed in U.S. Ser. No. 08/616,406, entitled "Olefin Polymer Blends for Hot Melt Adhesives", filed on Mar. 15, 1996 in the names of Parikh et al., and U.S. Ser. No. 08/615,750, entitled "Adhesives Comprising Olefin Polymers", filed on Mar. 14, 1996, in the names of Simmons, et. al. While these preferred hot melt adhesives are advantageous, industry is continually in need of alternate adhesive systems.

In some embodiments, ultra-low molecular weight ethylene polymers disclosed herein may be employed as an extending or modifying composition. Ultra-low molecular weight polymers employed will be either ethylene homopolymers or interpolymers of ethylene and a comonomer selected from the group consisting of C_3 -C_{20} alpha-olefins, styrene, alkyl-substituted styrene, tetrafluoroethylene, vinylbenzocyclobutane, non-conjugated dienes, and cycloalkenes.

EXAMPLES

General: All organometallic reactions and polymerizations were performed under a purified argon or nitrogen atmosphere in a Vacuum Atmospheres glove box, using glassware previously dried in a vacuum oven at 150°C. overnight. All solvents used were anhydrous, de-oxygenated and purified according to known techniques. All ligands and metal precursors were prepared according to procedures known to those of skill in the art, for example, under inert atmosphere conditions, etc. Ethylene/styrene copolymerizations were carried out in a parallel pressure reactor, which is fully described in pending U.S. Patent Applications No. 09/239,223, filed January 29, 1999, and WO 00/09255, and U.S. Patent No. 6,306,658.

High temperature Size Exclusion Chromatography (also known as gel permeation chromatography, "GPC") was performed using an automated "Rapid GPC" system as described in U.S. Patents 6,175,409, 6,260,407, and 6,294,388. A series of two 30 cm x 7.5 mm linear columns were used, with one column containing PLgel 10um, MixB and the other column containing PLgel 5um, MixC (available from Polymer Labs). The GPC system was calibrated using narrow polystyrene standards. The system was operated at a eluent flow rate of 1.5 mL/min and an oven temperature of 160°C. o-dichlorobenzene was used as the eluent. The polymer samples were dissolved 1,2,4-trichlorobenzene at a concentration of about 1 mg/mL. Between 40 μL and 200 μL of a polymer solution were injected into the system. The concentration of the polymer in the eluent was monitored using an evaporative light scattering detector. All of the molecular weight results obtained are relative to linear polystyrene standards.

Due to the low molecular weight of the ethylene-styrene copolymers produced by the catalyst systems described herein, the resolution obtainable using the Rapid GPC system is limited by the lower exclusion limit of the column material. Because the molecular weights of the products made in some embodiments of the invention are close to or below the lower size exclusion limit of the GPC columns, the M_w (weight average molecular weight) and especially the M_n (number average molecular weight) obtained by GPC are overestimated, while the polydispersity index (PDI = M_w/M_n) is underestimated, due to the lowest molecular weight fractions, which are below the size exclusion limit of the column material, eluting at approximately the same time as the higher molecular weight fractions which are at or slightly above the lower exclusion limit. The M_w and PDI shown in Table 4b illustrate this dependence of measured PDI on molecular weight. However, in some embodiments, this may not be the case.

1. An article of manufacture, comprising:
a copolymer of ethylene and vinyl aromatic monomer having a molecular weight of less than 15,000.

2. The article of manufacture of claim 1, wherein the copolymer is characterized by a backbone having a first and second terminal end group, the first terminal end group is a methyl group, the second terminal end group is a vinyl group, wherein the ratio of the terminal methyl group to the terminal vinyl group is 0.8:1 to 1:0.8.

3. The article of manufacture of claim 2, wherein the backbone of the copolymer is substantially free of a vinylidene group.

4. The article of manufacture of claim 1 or 2, wherein the article is a wax.

5. The article of manufacture of claim 1 or 2, wherein the article is a hot melt adhesive.

6. The article of manufacture of claim 1 or 2, wherein the article is an electrostatic toner.

7. The article of manufacture of claim 1 or 2, wherein the article is a lubricant.

8. The article of manufacture of claim 1 or 2, wherein the copolymer includes a functional group.

9. The article of manufacture of claim 8, wherein the functional group is a halogen, hydroxyl, anhydride, amine, amide, carboxylic acid, ester, ether, or nitrile group.

10. A method of functionalizing a polymer, comprising:
obtaining a copolymer of ethylene and vinyl aromatic monomer having a molecular weight of less than 15,000, the copolymer being characterized by a backbone having a first and second terminal end group, the first terminal end group being a methyl group, the second terminal end group being a vinyl group, wherein the ratio of the terminal methyl group to the terminal vinyl group is 0.8:1 to 1:0.8; and effectuating functionalization of the vinyl group to make a functionalized copolymer.

11. The method of claim 10, wherein the functionalization is chlorination.

12. The method of claim 10, wherein the functionalization is epoxidation.

13. The method of claim 10, wherein the functionalization is oxidation.

14. The method of claim 10, wherein the functionalization is carboxylation.

15. The method of claim 10, wherein the functionalization is sulfonation.